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FABRICATION AND CHARACTERIZATION OF POLY METACHLOROANILINE /MWCNTS ON TO CHTOSAN WITH C30B NANOCOMPOSITE FOR ELECTRICAL AND MORPHOLOGICAL PROPERTIES

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ABSTRACT

In the present study, we describe the synthesis of acid functionalized multiwalled carbon nanotube (MWCNT) which is grafted to chitosan (CH)/closite30B by first reacting the oxidized MWCNT with thionyl chloride to form acyl-chlorinated MWCNT and further grafted with poly metachloroaniline (PmClAn). MWCNT- PmClAn is subsequently dispersed in chitosan/C30B and covalently grafted to form MWCNT/ PmClAn -CH/C30B. We have characterized the structure of MWCNT/ PmClAn-CH/C30B composites by UV-visible spectrophotometer, scanning electron microscopy, transmission electron microscopy (TEM) and conductivity measurements. The unique performance of MWCNT composite, coupled with ease of fabrication shows great possibility for electrical applications as cathode materials in batteries and other electronic devices.

KEYWORDS: Poly Metachloroaniline, Chitosan, C30B, MWCNT, Nanocomposite & Electrical Properties

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Original Article

INTRODUCTION

Supercapacitors have garnered much attention as energy storage devices. Layered inorganic solid and conducting polymer nanocomposite is a unique combination at molecular level; they show novel mechanical, thermal and electrical properties[1]. Conducting polymer /MWCNT based nanocomposite have attached attention due to their great potential for application such as biosensor, capacitor, catalysts, gas sensor, and nanoelectronics[2,3]. Substituted conducting polymer polyaniline blends and composites such as chitosan/ PNEAn, chitosan/PNMAn[4], poly vinylidene fluoride/P2ClAn[5], Red Mud/P2ClAn[6], MoS_2/polyaniline[7], poly imide/ poly N-ethyl aniline[8], poly N-methylaniline/ CNT[9], and others have been reported respectively.

In this paper, we discuss the synthesis of a particular type of MWCNT-based nanocomposite using CH and PmClAn, and investigate its physical, chemical and electrical properties for different compositions. Chemical modifications of MWCNT- PmClAn -(CH-C30B) nanocomposite are confirmed using a number of material characterization techniques such as UV-visible spectrophotometer, SEM,TEM and conductivity.

EXPERIMENTAL

Materials

Multiwall carbon nanotube (>90% purification; 10-20nm diameter) was purchased from Cheap Tubes, USA. Poly Meta chloroaniline (PmClAn) was purchased from Aldrich, Chitosan (CS) and closite30B were purchased from Himedia. Other reagent and chemicals like HCL, HNO_3 and H_2SO_4 and ammonium persulfate

(APS), were of analytical grade

Carboxyl Group Functionalized MWCNT

MWCNTs was suspended in sulphuric acid and nitric acid mixture at 3:1 concentration and then refluxed for 45 min in an ultrasonic bath. After that the mixture was transformed to magnetically stirred and heated at 60°C for 24 h. This treatment provides carboxylic acid groups at defects in the surface of MWCNT[10]. The obtained c-MWCNTs was filtered by using 0.2-μm PTFE membrane filter and then washed with deionised water until the pH value was around 7 and dried at 60 °C for 24 h.

Synthesis of the Poly Metachloroaniline (PmClAn)–MWCNT Nanocomposite

The c-MWCNTs/ PmClAn nanocomposites were prepared via the *in situ* chemical oxidative polymerization of PmClAn in the presence of the f-MWCNTs: 5.0 ml PmClAn and a certain amount of f-MWCNTs (feeding ratio to PmClAn of 0.02:1, 0.5:1, 0.1:1, or 0.5:1) were added into 25 ml 1.0 mol/l HCL, respectively. Then 5 ml ethanol was added and ultrasonicated for 45 min to disperse the f-MWCNTs. 5ml of aqueous solution containing APS were added drop by drop to the above mixture over 20 min. The reaction vessel was maintained at 37^0C for 8 h. The prepared nanocomposite were filtered and washed with two to three times with distilled water and then ethanol, followed by vacuum drying at 45°C overnight. The products were denoted as f-MWCNTs/ PmClAn -2, f-MWCNTs/ PmClAn -5, f-MWCNTs/ PmClAn -10, or f-MWCNTs/ PmClAn -15 with the f-MWCNTs feeding ratio to PmClAn of 0.02:1, 0.5:1, 0.1:1, or 0.15:1, respectively.

Preparation of the CH/C30B/ (PmClAn –MWCNT) Nanocomposite Films

The (CH-C30B)/)f-MWCNTs/ PmClAn-10) nanocomposite films were obtained by following procedure. 1gm CH was prepared in 2% acetic acid and Cloisite 30B with 2.5% compositions based on chitosan were prepared and vigorously stirring at room temperature for 24 h to obtain homogeneous mixture. (CH-C30B) and (f-MWCNTs/ PmClAn -10) were suspended in double distilled H_2O with sonication for 30 min at 30°C, 40 kHz and 100 W. Subsequently, the above CH-C30B solutions were charged into (f-MWCNTs/ PmClAn -10) mixture and stirred at 1000 rpm for 1h and then sonicated for 30 min to facilitate the intercalation of CH-C30B and (f-MWCNTs/ PmClAn -10). Then, the (CH-C30B)/ (f-MWCNTs/ PmClAn -10) mixture were poured into a Petri dish (7 cm×13 cm) and the water was evaporated at 45°C by using oven. The standardized films were obtained with 40 μm thickness in Figure 1.The weight ratio of (CH-C30B) and (f-MWCNTs/ PmClAn -10) (1:1) to the total film is kept at 0, 0.2, 0.5, 1.0, 2.0 and 5.0 wt%.

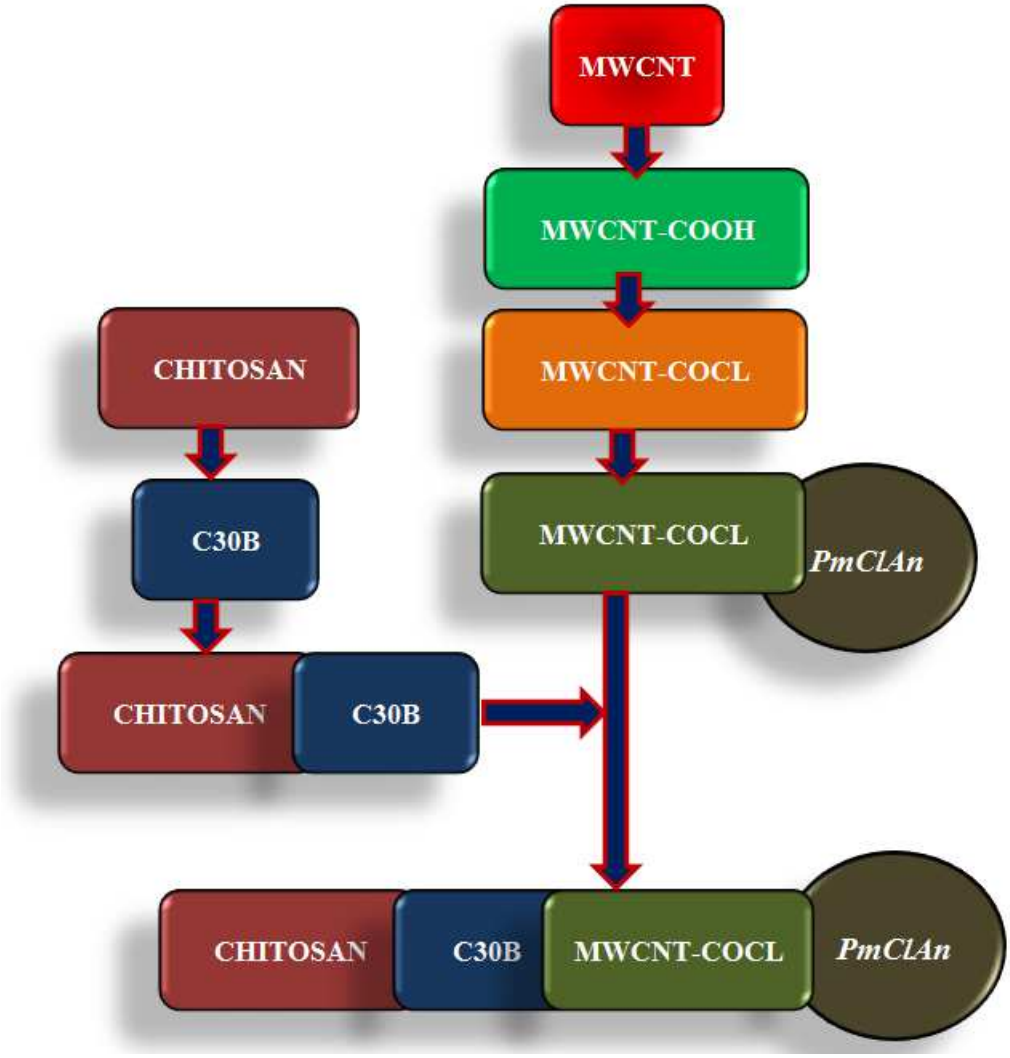

Figure 1: Schematically Represent Preparation of CH-C30B and f-MWCNTs/ PmClAn

MEASUREMENT

UV–vis Absorption Spectra Measurement

For the absorbance measurements the solids (in the untreated, as obtained, form) were dissolved in N-methylpyrrolidone (NMP) and the UV–vis spectra were recorded in the range 200–1000 nm. Then, hydrochloric acid was added to reduce the (co)polymer and the absorption spectra were recorded again. All the UV–vis measurements were performed

SEM

Morphology of the PmClAn/c-MWCNTS and CH /C30B/PmClAn –f-MWCNTs composite was investigated using a Philip XL 30 scanning electron microscope at an accelerating voltage of 25 kV. The sample was fractured at liquid nitrogen temperature and then was coated with a thin layer of gold before observation.

TEM

Transmission electron microscopy (TEM) experiments were performed on a Hitachi H-8100 electron microscope with an acceleration voltage of 200 kV.

Conductivity

The standard Van Der Pauw DC four probe method was used to measure the electron transport behavior of PmClAn/f-MWCNT composites. The samples of PmClAn and PmClAn/f- MWCNTs and CH /C30B/PmClAn –f-MWCNTs were pressed into pellet. The pellet was cut into a square. The square was placed on the four probe apparatus, providing a voltage for the corresponding electrical current could be obtained. The electrical conductivity of samples was calculated by the following formula:

$$\sigma\ (S/cm) = (2.44 \times 10/S) \times (I/E),$$

Where σ is the conductivity; *S* is the sample side area; *I* is the current passed through outer probes; *E* is the voltage drop across inner probes.

RESULTS AND DISCUSSIONS

UV-Visible Spectrophotometer

The UV–visible spectra of the PmClAn/f-MWCNTs in NMP solutions are presented in Figure 2. The major peak at about 324 and 615 nm is observed, which is assigned to the excitation of the benzene and quinoid segments on the polyemeraldine chain, respectively. In order to obtain the doped PmClAn/ f-MWCNTs, one drop of 35 wt % HCl is added to the above solutions. The absorption peaks at 321 and 435nm are formed. The absorption peak at about 321 nm can be ascribed to π–π* transition of the benzenoid rings, whereas the peaks at around 411 nm can be attributed to polaron–π* and π–polaron transition.

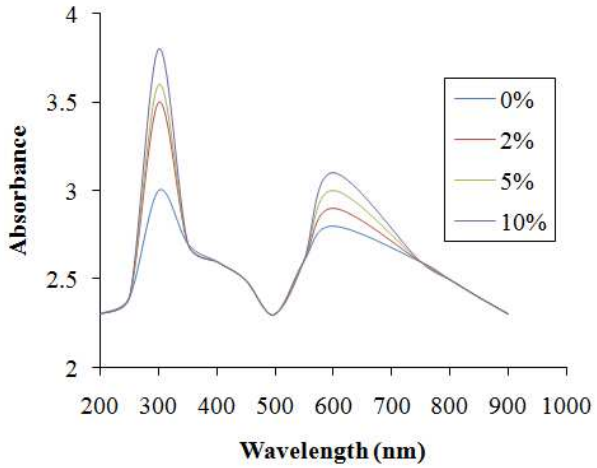

Figure 2: UV–vis Spectra of PmClAn/f-MWCNT Composites in NMP Solutions: a. 0 wt% f- MWCNTs; b. 2 wt% f- MWCNTs; c. 5 wt% f-MWCNTs; d. 10 wt% f-MWCNTs)

SEM

The bonding and dispersion of the f-MWCNT to the pure PmClAn and CH-C30B composite are important issue for preparing of CH /C30B-PmClAn /f-MWCNTs nanocomposite. The morphological structure of composite was analysed

within reach into the surface characteristics of the CH /C30B-PmClAn /f-MWCNTs nanocomposite. Figure 3 shows the SEM image of the CH /C30B-PmClAn /MWCNTs nanocomposite and it can be seen that f-MWCNTs was well distributed within the nanocomposite and homogeneously dispersed[11].

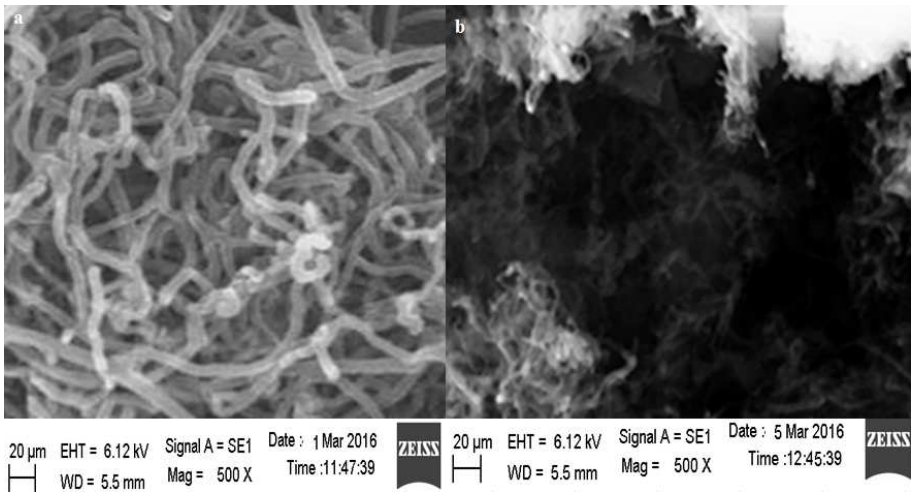

Figure 3: SEM Images of a. f-MWCNT/ PmClAn; b.CH /C30B/ PmClAn –MWCNTs-10

TEM

The TEM of CH /C30B/ PmClAn –MWCNTs composites are presented in Figure 4. From result, it can be done that CH /C30B /PmClAn –f-MWCNTs composite is representative core–shell structure, f-MWCNT was served as the core and dispersed into the composite[12, 13]

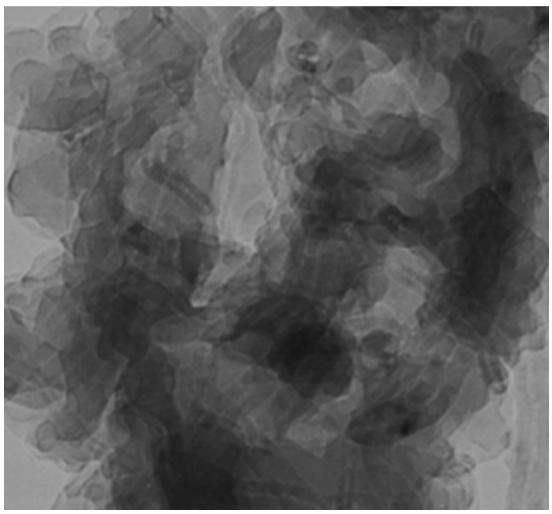

Figure 4: TEM Images of CH /C30B /PmClAn –f-MWCNTs

Electrical Conductivity

Figure 5 shows the electrical conductivity of the f-MWCNTs/ PmClAn and MWCNT/ PmClAn-CH/C30B composites measured with the standard four probes method at room temperature. It is noteworthy that all the electrical conductivity values of the f-MWCNTs/ PmClAn and MWCNT/ PmClAn-CH/C30B composites were higher than for f-MWCNT. It was demonstrated that highest electrical conductivity of 19.43 S/cm for the f-MWCNTs/PmClAn-10 composite, because the electrons could transport through the overlapped PmClAn contact between the f-MWCNT/

PmClAn bundles[14, 15]. However, when the feeding ratio of the f-MWCNTs increased further, the conductivity of the composites showed a downward trend. But in comparing in between MWCNTs/ PmClAn and MWCNT/ PmClAn-CH/C30B, the electrical conductivity of MWCNTs/ PmClAn is higher than MWCNT/ PmClAn-CH/C30B because the addition of CH /C30B composite is insulating materials.

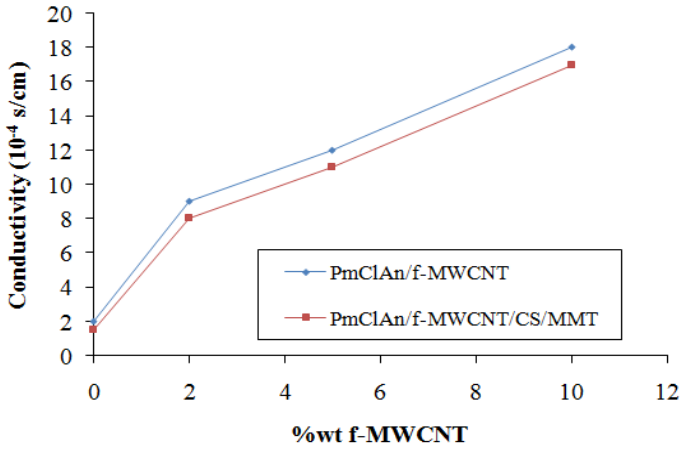

Figure 5: Conductivity Versus the Weight Percent of f-MWCNT/PmClAn and MWCNT/ PmClAn-CH/C30B Composites

CONCLUSIONS

In summary, we have successfully fabricated MWCNT-PmClAn /-CH/C30B as a new form of MWCNT-based nanocomposite, and investigated its morphological and electrical properties with various compositions. Material characterizations performed using various measurements such as SEM and TEM measurements indicate homogeneous dispersion of MWCNT-PmClAn nano-platelets within the CH/C30B polymer matrix. The electrical conductivity of the MWCNT-PmClAn/-CH/C30B nanocomposite has also been investigated. Increase in conductivity has been observed with increasing f-MWCNT volume fraction. Due to the prominent electrical properties of PmClAn and nanodimension of MWCNT-PmClAn/-CH/C30B, such nanocomposites can find applications as cathode materials in batteries, and electronic devices.

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REFERENCES

1. *Lee D, Char K, Lee S. W, ParkY. W. J, Mater. Chem, 13 (2003) 2942–2947.*
2. *Sanches E. A, Soares J. C, Iost R. M, Marangoni V. S, Trovati G., Batista T, Mafud A. C, Zucolotto V, Mascarenhas Y. P, J.Nano Mat. 2011, 1-45*
3. *Pande S, Swaruparani H, Bedre M. D, Bhat R, Deshpande R, Venkataraman A, Nanoscience and Nanotechnology, 2 (2012) 90-98.*
4. *Yavuz A. G, Uygun A, Bhethanabotla V. R, Carbohydr. Polym. 75 (2009) 448–453.*

5. *Gök A, Oğuz I, J. Appl. Polym. Sci. 99 (2006) 2101–2108.*
6. *Bissessur R, White W, Dahn D. C, Mater. Lett. 60 (2006) 248 – 251.*
7. *Bissessur R, White W, Mater. Chem. Phys. 99 (2006) 214–219.*
8. *Iroh J. O, Levine K, Shah K, Zhu Y, Donley M, Mantz R, Johnson J, Voevodin N. N, Balbyshev V. N and Khramov A. N., Surf. Eng, 20 (2004) 93-98.*
9. *Lu X, Zheng J, Chao D, Chen J, Zhang W, Wei Y, J. Appl. Polym. Sci. 100 (2006) 2356-2361.*
10. *Choudhury A, Synthetic Metals, 188 (2014) 13-20*
11. *Abbasi M, Mahdi Habibi M, Journal of the Taiwan Institute of Chemical Engineers, 62(2016) 112-121*
12. *Aroon M.A, Ismail A.F, Montazer-Rahmati M.M, Matsuura T, Journal of Membrane Science, 364(2010) 309-317*
13. *Marcia P. M. C, Ferreira I. L. D.M, Macedo Cruz M. T.D, Carbohydrate Polymers, 146 (2016) 123-130*
14. *Dai L, Xu Y, Gal J.Y, Lu X. and Wu H, Polymer International, 51(2002), 547–554,*
15. *Wang L, Li Y, Wang Q, Zou L, Ye B, Sensors and Actuators B: Chemical, 228)2016) 214-220.*